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A STUDY OF CERTAIN CARBOHYDRATE DEGRADATIONS DURING SULFITE PULPING

INTRODUCTION

At present, the knowledge of the factors which contribute to the degradation of carbohydrate polymers during pulping is very limited. Such knowledge is limited chiefly to the effects of the hydronium ion during acidic processes and, to lesser extents, to the effects of the hydroxide ion, oxygen, and the delignifying chemical. Although several pathways may be postulated for the degradation of glycosidic bonds by the hydronium ion, complex electronic, configurational, and thermodynamic interactions make difficult the choice of the actual pathways which do occur under a given set of circumstances (1, 2).

Less is known of the mechanisms of carbohydrate degradation which occur during the various alkaline cooking processes. The alkaline peeling reaction has been studied at various temperatures (3) and complex atomic rearrangements and migrations have been proposed to explain this reaction and the formation of the various saccharinic acids. The scission of glycosidic bonds which occurs in alkaline media (4) may proceed by several different mechanisms. The degradation of β-methyl glucoside in alkali at different temperatures and pH levels has been studied by Brooks (5). It is possible, for example, that the cleavages brought about by the viscose aging process may occur by mechanisms different from those

that occur at elevated temperatures during alkaline cooks (5, 6). The latter degradation also seems to be influenced by factors affecting the glycosidic bond (5, 7).

Other degradations may occur during pulping, and these include oxidative and reductive effects brought about by the active delignifying chemicals. Some of these may be harmful or beneficial, as is the oxidation which presumably occurs during the polysulfide cooking process (8, 9).

The present research was initiated to continue the investigation of degradations which occur during pulping at different pH levels (10). A number of simplifications were introduced into the study. In most instances, the yield and the viscosity measurements were employed as a measure of pulp degradation, and viscosity was assumed to be closely related to the cleavage of carbohydrate molecules.

EXPERIMENTAL

The cooking liquors used in this investigation were based upon a sodium sulfite solution (118 g. per liter), and the pH of the solution was adjusted to about 8.5 with 10 g. of sodium bicarbonate; no additions were made for pH 8.9-9.2; pH 10-10.5 was reached with the addition of 9.6 g. of sodium carbonate, pH 12-12.5 with 9.6 g. of sodium carbonate and sodium sulfide, and higher pH levels with the addition of 9.6 g. of sodium sulfide and 28.7 g. of sodium hydroxide. The presence or absence of 9.6 g. of sodium carbonate had little effect upon the pH or degradative ability of the latter solution.

In certain cooks, liquors were buffered with sodium sulfite-free salts. These include: 289 g./liter of sodium phosphate dodecahydrate to give pH 11;

80 g./liter of sodium phosphate dodecahydrate, 56 g./liter sodium bicarbonate, and 40 g./liter of sodium carbonate to give pH 9.8; 60.5 g./liter of sodium carbonate and 9.6 g./liter of sodium bicarbonate to give pH 9; and 200 g./liter of sodium acid arsenate heptahydrate and 84 g./liter of sodium bicarbonate to give pH 8.

Commercial white spruce chips were employed in this investigation, and control experiments showed black spruce to be degraded in a similar manner. The chips were cooked in microdigesters according to the procedure described by Thode, Peckham, and Daleski (11) using a 90-minute cycle to maximum temperature. Acetylation-grade cotton linters were also cooked in the microdigesters, while the reactions of 4-O-methylglucuronoxylan and alkali-soluble cellulose were carried out in still smaller digesters according to procedures described elsewhere (5, 12).

Hydrocellulose was prepared by reacting viscose-grade linters with 0.5N sulfuric acid at 100°C. for 8 hours. Alkali-soluble cellulose was prepared by a modification of Davidson's method (13) from this cellulose by freezing it with 10% sodium hydroxide at 10% consistency. After thawing, the mixture became a translucent, jellylike, viscous mass which was centrifuged, washed with an equal volume of 10% sodium hydroxide, and centrifuged to give an alkali-soluble cellulose in 40% yield. Aliquots of the freshly extracted alkali-soluble cellulose were adjusted to the desired pH for cooking with sulfur dioxide gas, and the resulting cellulosic suspension was transferred to the small digesters described above (12).

The 4-O-methylglucuronoxylans and the soluble (or dispersed) glucans were recovered after cooking by neutralizing the liquors with acetic acid, dialyzing by a standard procedure (11) to remove sodium salts, and freeze drying to give colorless, fluffy products. The polymers were weighed for yield determinations, and viscosities were measured in molar cupriethylenediamine.

RESULTS AND DISCUSSION

In previous publications (10, 14), the change in viscosity of pulps cooked to 10 or 20 permanganate number at different levels of cooking liquor pH was examined. The assumption was made in those earlier studies that the average of the pH's of the cooking liquors before and after cooking represented an average pH not too different from the actual pH of the cooking liquor and that any differences would tend to disappear of the pH levels were used in a comparative rather than an absolute sense. Recent research by Ingruber (15) on aqueous systems of sodium hydroxide and sulfur dioxide at different pH levels and temperatures up to 160°C. tends to confirm some aspects of this generalization. Another assumption was that since all the pulps had very similar, although not identical, yields as well as uniformly low hemicellulose contents, the viscosities of the pulps might therefore be considered to be closely related to the average degree of polymerization of the cellulose of the pulps. No information was obtained concerning the distribution of degrees of polymerization of the carbohydrate material of the pulps.

The results of this study, reviewed in Fig. 1, indicate that as the average pH of the cooking liquor was increased from that of the acid sulfite liquor (pH 1.8) toward the bisulfite (pH 3.7) and sulfite (pH 5.6), increasing degradation as reflected by a loss of pulp viscosity resulted. The lower viscosity of the bisulfite pulp has been explained to be the result of the longer reaction times and temperatures of the bisulfite process (16). The low viscosities of the kraft and modified kraft pulps (~ pH 12) compared to those pulps prepared by cooking at pH 11 are consistent with the assumption that increasing carbohydrate degradation should accompany increasing pH, "effective alkali," or hydroxyl ion concentration. Brooks has found that the degradation of β-methylxyloside in alkali at a given

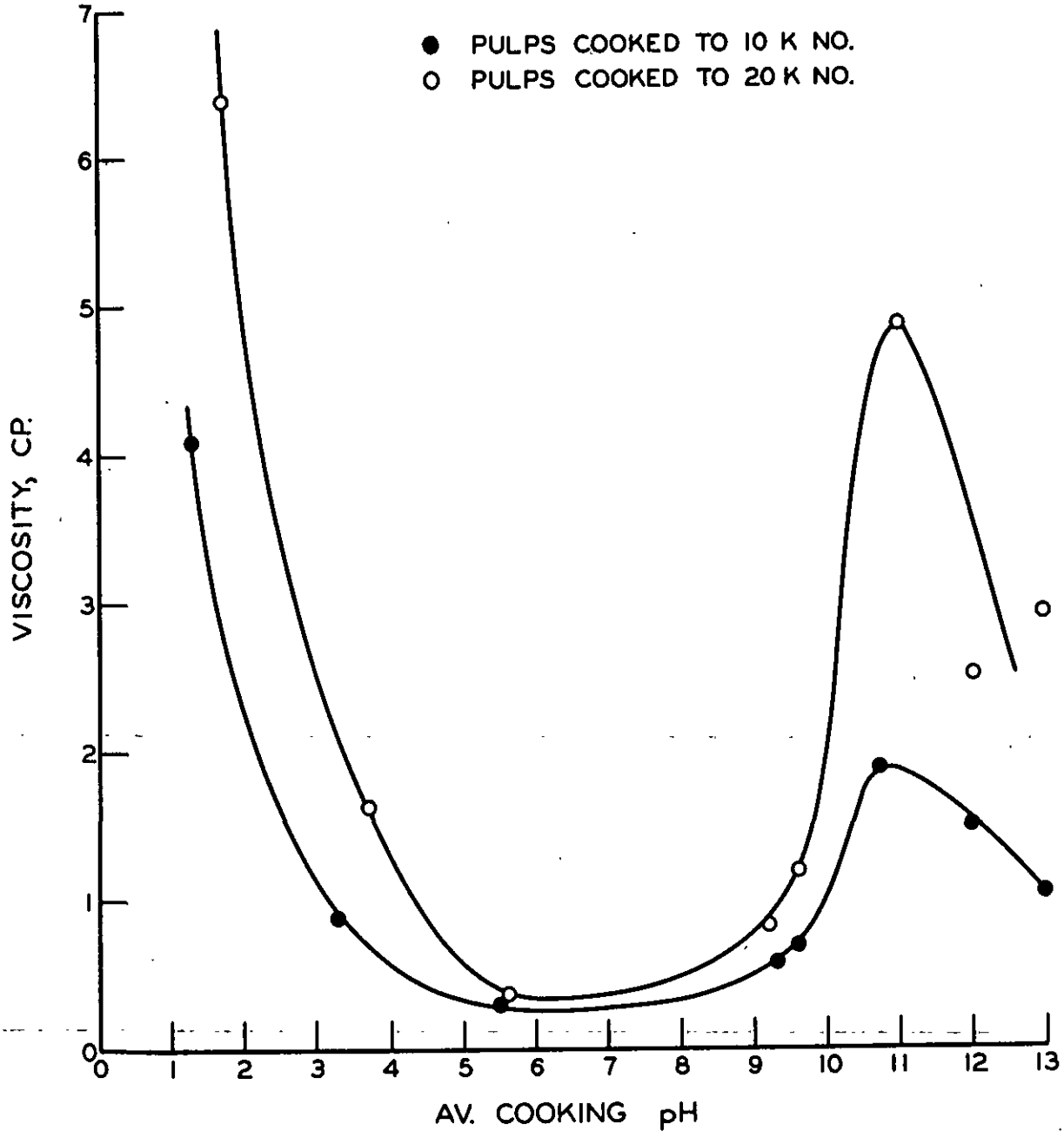

Figure 1. Variation of Viscosity of Pulps with Average pH of Cooking Liquor

temperature is dependent upon the pH of the alkaline cooking liquor. The loss of pulp viscosity which occurs when the average pH of the cooking liquor is decreased below pH 11 cannot be explained on this basis, however.

Since the temperature and times of reaction of the cooks shown in Fig. 1 were not identical, a second series of cooks was conducted at 180°C. and different pH levels for eight and nine hours. The results shown in Fig. 2 are typical of those which can be obtained from white or black spruce or presumably from any other conifer. The results support the earlier work and show that pulp degradation does increase when the pH of the cooking liquor is decreased from pH 11 to 5.

Mithel, Webster, and Rapson (17) found a similar decrease in pulp viscosity when an acetylation-grade wood pulp was heated at elevated temperatures in aqueous phosphate buffers between pH 5 and 8. These researchers rationalized their results by assuming that the hydronium ion concentration of the liquor determined the amount of hydrolytic degradation of the cellulose at any temperature, that the degradation products were acidic and caused a drop in liquor pH, and that this hydrolytic effect was superimposed upon a solubility effect which was considered to be a function of the hydroxyl ion concentration.

It is possible to examine these assumptions in the light of the present research. The optimum pulp viscosity shown in Fig. 2 occurs somewhere near pH 11, and it would correspond to a point where the degradation wrought upon the cellulose by the hydronium ion was equal to the degradation caused by the hydroxide ion. Thus, it might be postulated that an increase in pH from 11 toward 14 results in a loss of pulp viscosity due to the degradative influences associated with the increasing concentration of hydroxyl ion, whereas the loss of viscosity resulting from the decrease in pH from 11 is due to the increasing degradative effect of the hydronium ion.

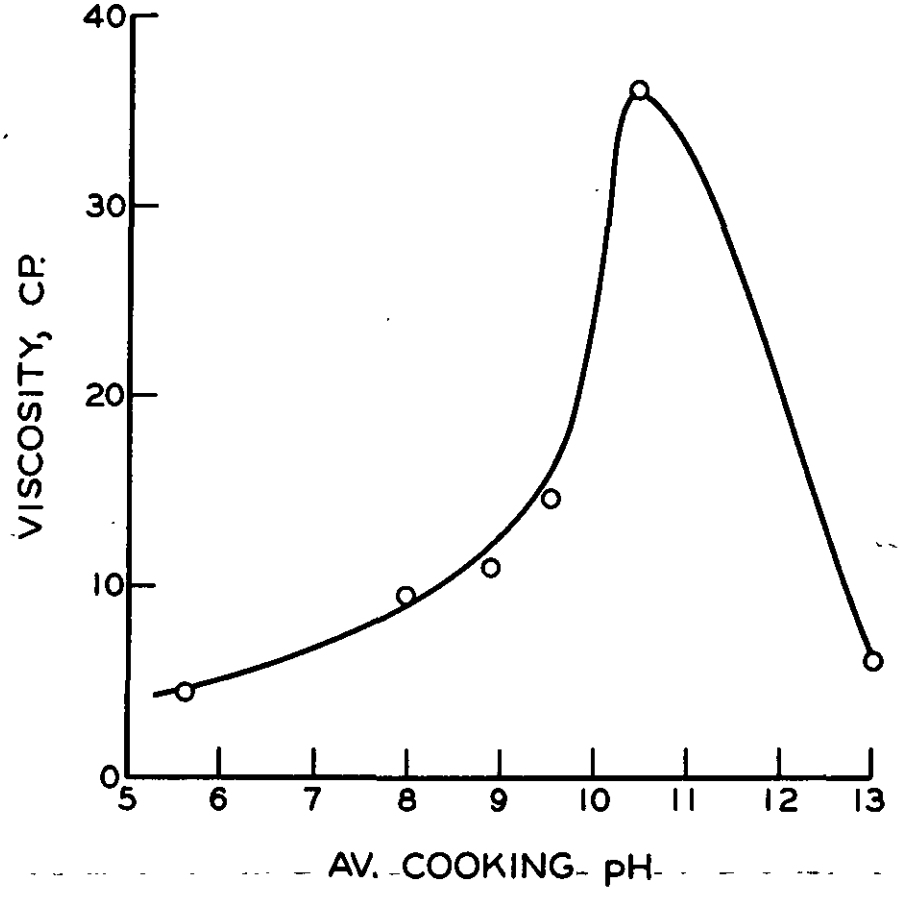

Fig. 2. Effect of Liquor pH on Viscosity of Spruce Sulfite Pulp Cooked 7 Hours at 170°C.

A comparison of the pulps cooked at pH 1.8, 5.6, and 9.2 indicates the viscosity of the last two to be about one twentieth and one eighth, respectively, of the viscosity of the acid sulfite pulp. This observation suggests that extensive additional hydrolytic damage by the hydronium ion must have occured at the higher pH levels of 5.6 and 9.2 and might be due to the longer times and higher temperatures of reaction proposed in the literature (16, 17) to explain such phenomena. According to Table I, the acid-catalyzed hydrolysis of the glycosidic bonds must have been sufficiently severe in the case of the acid sulfite pulp to cleave all acid-labile arabofuranose and terminal galactopyranose units from the 4-O-methylglucuronoarabinoxylan, galactoglucomannan, and glucomannan polymers of that pulp. The hydrolytic degradation wrought upon the pulp cooked at pH 5.6 was also sufficient to remove all acid-labile sugars and to decrease the pulp viscosity to about one twentieth of that of the acid sulfite pulp. The viscosity of the pulp cooked at pH 9.2, although greater than the aforementioned pulp, was about one eighth that of the acid sulfite and about one half that of the bisulfite pulp. Insufficient hydronium ion was present to remove all the acid-labile arabinose and galactose units from this pulp despite the fact that the pulp viscosity was less than those of the acid sulfite and bisulfite pulps. Polysaccharide analysis showed the presence of 4-O-methylglucuronoarabinoxylan and galactoglucomannan in these alkaline pulps (10).

In an earlier research (10), it was assumed that the cellulosic degradation occurring in the neighborhood of pH 8-9 was due to some special character of wood pulp. The hypothesis is shown to be in error since cotton linters reacted with liquors of different pH also exhibits a viscosity maximum near pH 10, as is shown in Fig. 3. The change in viscosity for cotton linters cooked in liquors of different average pH and different temperatures is also given in Fig. 3, and shows the temperature dependence of the viscosity maximum. The results suggest

TABLE I

CARBOHYDRATE COMPOSITION OF BLACK SPRUCE PULPS COOKED AT DIFFERENT pH LEVELS

	Average pH					
	1.8	3.7	5.6	9.2	9.6	11.0
Viscosity	63.8	16.2	3.4	8.1	12.0	48.7
Yield, % of wood	53.3	50.3	46.8	45.0	47.1	49.3
Galactan, % of wood	0	0	0	0.35	0.37	0.35
Mannan, % of wood	3.4	3.7	4.0	3.0	2.6	2.4
Araban, % of wood	0	0	0	0.43	0.48	0.47
Xylan, % of wood	2.7	3.1	2.7	3.3	3.4	3.2

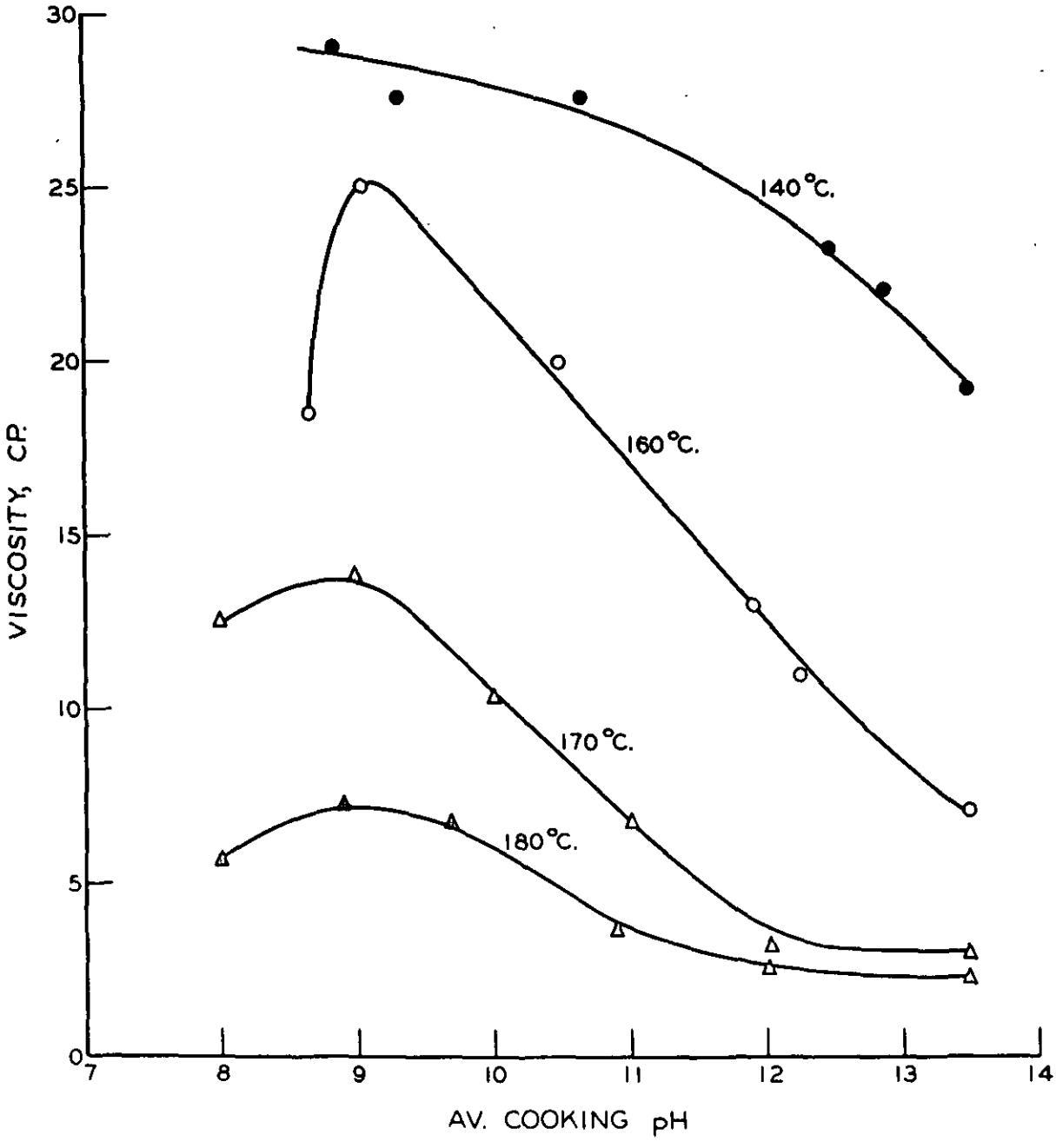

Figure 3. Effect of pH and Temperature on Viscosity of Cotton Linters (4-hr. Cook)

that below about 140°C., pulp degradation between pH 8 and 14 varies with the hydroxide ion concentration. At higher temperatures, a maximum viscosity appears between pH 8 and 14 which seems to shift to higher pH levels as the cooking temperature is increased. The yields of the linters pulps were all greater than 90%, suggesting that little extractive fractionation had occurred.

The effect of the duration of the cooking reaction upon the linters viscosity is given in Fig. 4. The cooks plotted were conducted at 180°C., and analogous plots were obtained at 170 and 160°C. levels of cooking. The longer reaction times result in lower pulp viscosities and a slight increase in the pH at which the maximum viscosity occurs. The results demonstrate that the behavior of the cellulose during pulping at different pH levels is not due to any influence on the part of some component of the wood but seems to be a characteristic of cellulose.

A comparison of 4-O-methylglucuronoxylan cooked at different pH levels and with different buffering solutions is given in Fig. 5 and 6. The variation of yield with cooking pH shown in Fig. 5 is a continuously decreasing curve with no suggestion of a maximum yield occurring at an intermediate cooking pH. The loss of viscosity of the polymers cooked at different pH levels using sodium sulfite liquors buffered to different pH levels is given in Fig. 6. Once again, no suggestion of a viscosity maximum was apparent. A second series of cooks was conducted using buffers composed of carbonate, phosphate, and arsenate ions instead of sulfite ions. A viscosity curve similar to the previous one was obtained, but at a 10% lower level, suggesting that alkaline sulfur dioxide solutions may have a slight stabilizing influence upon the chain cleavage mechanisms which occur in alkali. This phenomenon might be related to the formation

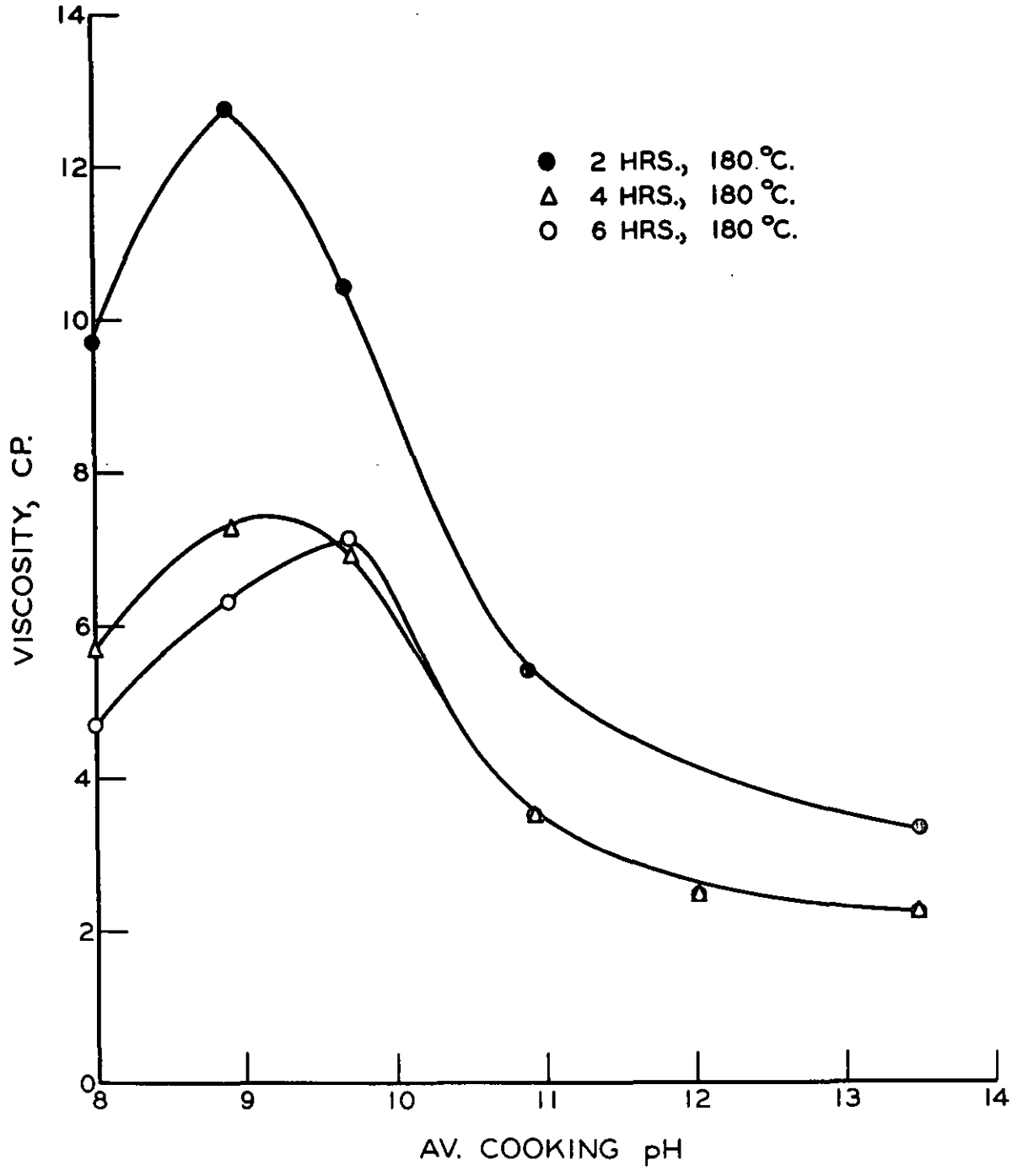

Figure 4. Effect of pH and Reaction Time on Viscosity of Cotton Linters (180°C. Cook)

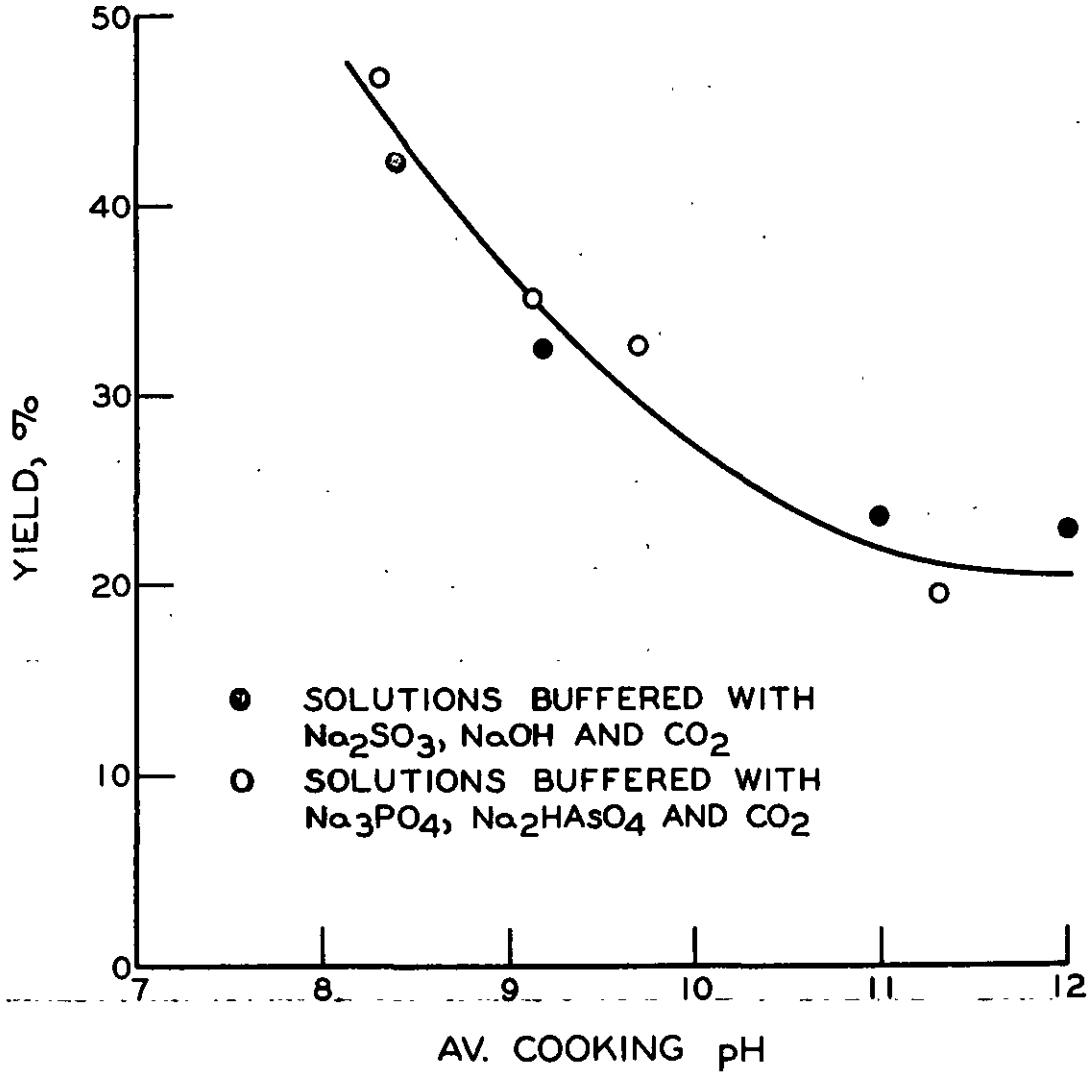

Figure 5. Effect of pH on Yield of 4-O-Methylglucuronoxylan (170°C. Cook)

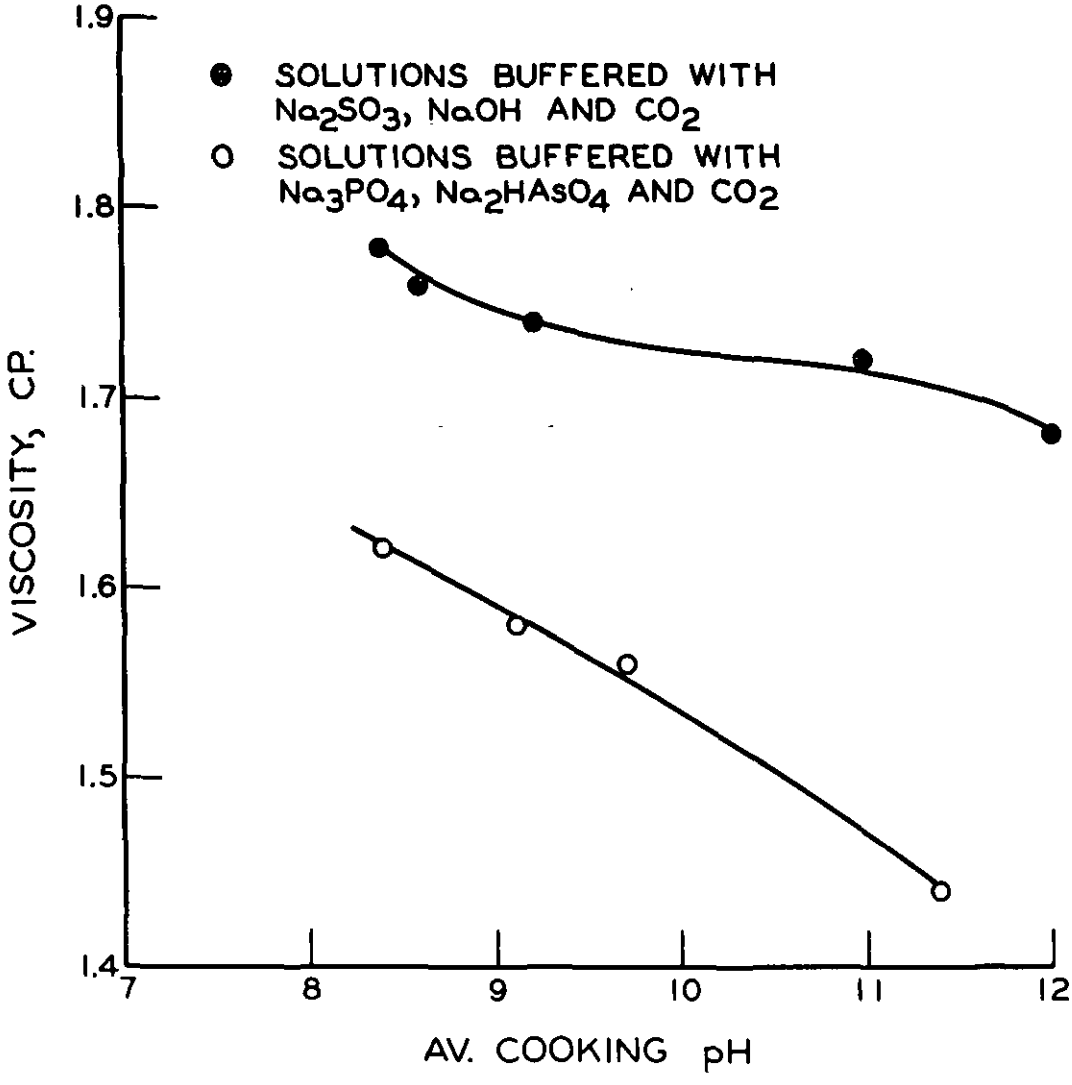

Figure 6. Effect of pH on Viscosity of 4-O-Methylglucuronoxylan (170° Cook)

of relatively alkali-stable terminal xylonic acids by the oxidation of the terminal reducing group of the xylan chain by sodium sulfite (18).

The difference in behavior between the cellulose and the 4-O-methylglucuronoxylan cooked at different pH levels in sulfite liquors is not due to any difference in the composition of the liquors. Unlike cellulose, the 4-O-methylglucuronoxylan is not seriously degraded at neutral pH levels, suggesting either reversal in the relative stability of the xylose-xylose and glucose-glucose glycosidic bonds at certain pH levels or that a difference in hydronium ion activity occurs in the neighborhood of the two polymers.

A comparison of the change in viscosity of cotton linters and dispersed cellulose in alkaline solutions of different pH and at 180°C. is given in Fig. 7. The dispersed cellulose does not exhibit a marked viscosity maximum similar to the cotton linters samples, and it is concluded that the two samples are behaving differently toward the cooking liquor. The dispersed cellulose does exhibit a degradation curve similar but not identical to the 4-O-methylglucuronoxylan shown in Fig. 6, but shows a leveling off at lower cooking pH. This behavior might be expected if the dispersed cellulose were not completely in solution but consisted of large gel aggregates dispersed in the alkali. It would exhibit properties intermediate between the soluble xylan and the insoluble cotton linters cellulose.

If this assumption is true, an explanation for the behavior of these polysaccharides can be formulated. The hemicelluloses would have been subjected to an aqueous environment in the neighborhood of pH 8 to 14, which would have exercised some control over the hydronium ion environment about the polymer. The cotton linters or wood cellulose, on the other hand, would have certain molecules in inaccessible regions which were not in contact with the cooking

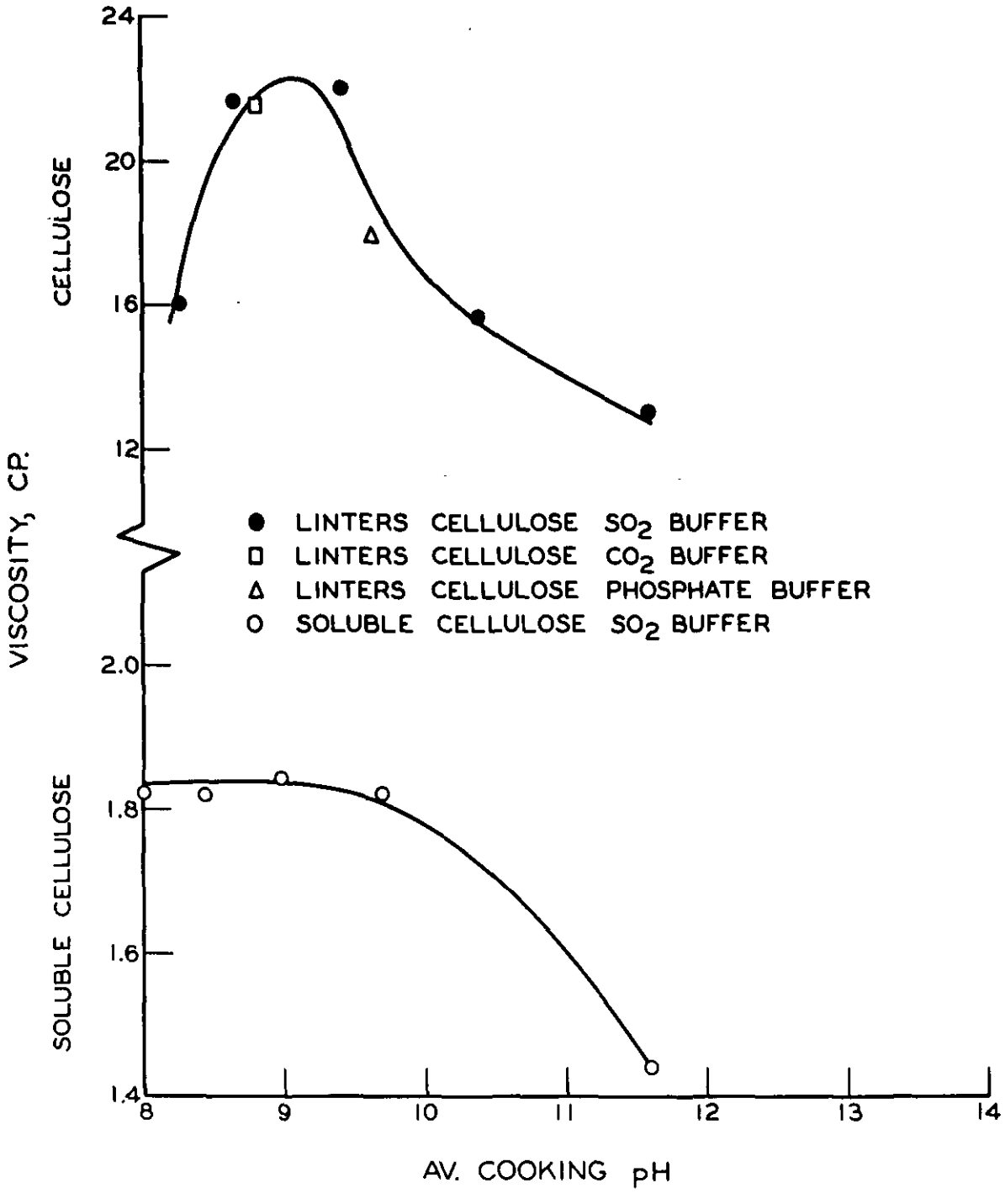

Figure 7. Effect of pH on Viscosity of Cotton Linters and Soluble Cellulose at 180°C.

liquor. The extent of this inaccessible region would not be constant, but would depend inversely upon the pH of the liquor.

Any hydronium ion introduced in the inaccessible and/or highly crystalline regions would result in a region of high acidity, which might not be buffered by the cooking liquor. Since acidic products and water can result from the pyrolysis of cellulose in the presence of water [(17), literature surveys (19) and (20)], and since there is no reason to expect pyrolytic degradation to predominate mostly in the accessible regions of cellulose, it is possible that acids may be found in those portions of the cellulose fiber which are not accessible to the buffered cooking liquor. At elevated temperatures, these acids could degrade the surrounding cellulose. The possibility exists that the small amounts of air retained by the wood fibers could also bring about the pyrolytic oxidation of carbohydrates to organic acids at pulping temperatures.

When more alkaline liquors are employed, increasing penetration of the cellulose (21) and more efficient neutralization or buffering of the degradation products should result. The degradation brought about by the pyrolytic degradation products of cellulose should become less as the pH of the cooking liquor increases until a point is reached where the degradation caused by the alkaline cooking liquor will be equal to the degradations caused by the remaining unbuffered hydronium ion. A further increase of the cooking liquor pH will result in increasing pulp degradation.

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PAGE 112 TO 132
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MACERATION (PULPING) OF SMALL WOOD SAMPLES

Introduction

The maceration, or pulping, of small samples of wood and other vegetable materials for use in fiber measurements and microscopic examination is widely used throughout the world. Probably the most generally successful maceration procedure for woody tissue is the chlorite procedure described by Spearin and Isenberg (1). To the best of our knowledge the procedure is rugged and reliable, and is not unduly hazardous when used without arbitrary modifications.

An adaptation of the Spearin and Isenberg procedure has been used successfully for some time by the Cytology Laboratory at the Institute. However, on April 4, 1967, an explosion occurred in the Cytology Laboratory during the chloriting of a set of wood samples. The explosion was the result, apparently, of the addition of 30 drops of glacial acetic acid to 10 g. of solid sodium chlorite in a test tube along with the wood wafers to be delignified. It was customary to add 30 ml. of water to this mixture after which the samples were placed in an oil bath at 90° for 8 hours. It should be noted that the order of addition of reactants is critical (1), and should never involve the contact of any organic substance, such as glacial acetic acid, with solid sodium chlorite.

The objective of the work described in this report was to develop an adaptation of the Spearin and Isenberg (1) procedure which might be at least as efficient and possibly somewhat easier to use.

Discussion

Maceration of Wood with Chlorite
Revised Procedures

The general procedure of Spearin and Isenberg (1) was employed in developing two procedures involving the maceration of wood wafers (10 mm. in diameter x 1 mm. thickness). The sample size was less than 1 g. of airdry wood; several variables were explored briefly.

The procedures differ chiefly in that No. I is sufficiently severe that the wafers are readily fiberized (pulped) when shaken vigorously by hand in water, whereas, No. II includes a step in which the delignified wafers are steeped in dilute alkali before the final fiberizing step. Procedure No. I requires a higher ratio of sodium chlorite to wood, and a longer heating period than procedure No. II. Either procedure appears to be suitable for the maceration of small amounts (less than 1 g. airdry) of wood in the form of thin chips or "match sticks" (1/8" x 1/8" x 3/4").

Several species of both hardwoods and softwoods were included in the study and all were readily macerated by either procedure except Austrian pine compression wood which pulped readily only by procedure No. II.

No attempt was made to remove extractives although in some cases this may be helpful if maceration is difficult, otherwise.

One experiment involved an alkaline pretreatment but the wafers were

more difficult to macerate than untreated wafers. Hence, an alkaline pre-treatment is not recommended.

Degassing the wafers as recommended by Spearin and Isenberg afforded no advantage. Possibly gaseous chlorine dioxide diffuses into the wood, filling the lumens and other spaces whether or not the wood is initially degassed. Therefore, degassing would appear to be unnecessary in the chlorite procedure for the maceration of wood wafers.

It is strongly recommended that a steam bath, rather than an oil bath as employed originally by the Cytology Laboratory, should be used to heat the samples. This would eliminate the explosion hazard of accidental contact of hot oil with sodium chlorite.

Attempted Maceration of Wood Wafers with Peroxyacetic Acid

One attempt was made to adapt the general procedure for delignification with peroxyacetic acid as described by Leopold (2) to the maceration of wood wafers. The results were unsatisfactory and the method was not investigated further. The chief problem appeared to involve the unsufficient penetration of the reagent into the wafers. After four hours' treatment, the exterior of the wafer was readily fiberized while the "core" remained incompletely delignified.

Revised Procedure I.

1. Prepare a stock solution of approximately 0.5 M acetic acid (30 ml. glacial acetic acid diluted with water to 1 liter).

2. Immediately before use, in a well-ventilated hood prepare an amount of the sodium chlorite reagent as required for each set of samples. The reagent is approximately 2.75 M sodium chlorite (250 g. of sodium chlorite per liter of solution) in 0.5 M acetic acid (Step 1). Each sample requires a total of 15 ml. of reagent containing 3.8 g. of sodium chlorite for samples composed of less than 1 g. of wood.

   Example: Assume a set of 10 samples which would require a total of 150 ml. of reagent. It may be advantageous to prepare enough reagent for one more than the actual number of samples to compensate for small errors in measurement. To a 250 ml. Erlenmeyer flask, bearing a wax pencil mark at the 150 ml. level, place 38 g. of solid sodium chlorite and dilute to the 150 ml. mark with 0.5 M acetic acid (Step 1).

   When the sodium chlorite is completely dissolved invert a small Erlenmeyer in the mouth of the flask to form a loose closure.

   Caution! Never prepare the reagent in a stoppered bottle or flask! Never pipette chlorite solutions by mouth! Use a graduated cylinder or an automatic dispensing device.*

   The reagent soon becomes dark brown in color, and yellow chlorine dioxide fills the space above the liquid. Prepared in this way, the reagent may be stored for 2-4 hours in the hood at room temperature and used as directed in the delignification schedule.

*Such a device is the "Cantipette" dispenser, Chemical Rubber Company, Cleveland, Ohio.

All unused reagent must be diluted with water and poured into the sewer before the end of each day!

3. Place the wafers of each specimen in a large test tube (25 x 190 mm.) with a 10 ml. Erlenmeyer flask inverted in the mouth of each test tube as a loose closure.
4. Pour 5 ml. of the chlorite reagent (Step 2) into each test tube and place the test tubes in a 1 liter beaker which contains 200 ml. of hot water. (When loaded, the level of water in the beaker should be 1-2 cm. higher than the level of liquid in the test tubes.)
5. Place the beaker loaded with test tubes on a steam bath and heat the samples for one hour after the temperature inside the test tubes reaches 70-75°. Occasionally shake the test tubes lightly during the heating period.
6. Add 5 ml. of reagent to each sample and continue the heating for 2 hours more, then add a third portion of 5 ml. of reagent and continue heating for the final two hours. Thus, each sample of wafers is treated with a total of 15 ml. of reagent and is heated for a total of 5 hours.
7. Cool the test tubes in cold water.
8. Pulp the wafers by the procedure described under "Fiber Washing and Stain" in Revised Method of Fiber Measurements, Cytology Laboratory, I.P.C., April 1967.

Revised Procedure II.

1. Prepare stock solutions as follows:

   0.5 M acetic acid (30 ml. glacial acetic acid diluted to 1 liter).

   0.2 M sodium hydroxide (8 g. solid sodium hydroxide dissolved in water and diluted to 1 liter).

2. Immediately before use, in a well-ventilated hood prepare an amount of the sodium chlorite reagent as required for each set of samples. The reagent is approximately 2.75 M sodium chlorite (250 g. of $NaClO_2$ per liter of solution) in 0.5 M acetic acid (Step 1). Each sample requires a total of 10 ml. of reagent containing 2.5 g. of sodium chlorite for samples composed of less than 1 g. of wood.

   Example: Assume a set of 10 samples which would require a total of 100 ml. of reagent. It may be advantageous to prepare enough reagent for one more than the number of samples to compensate for small errors in measurement. In a 125 ml. Erlenmeyer flask, bearing a wax pencil mark at the 100 ml. level, place 25 g. of solid sodium chlorite and dilute to the 100 ml. mark with 0.5 M acetic acid. When the sodium chlorite is completely dissolved, insert a small Erlenmeyer in the mouth of the flask to form a loose closure.

   Caution: Never prepare the reagent in a stoppered bottle or flask! Never pipette chlorite solutions by mouth! Use a graduated cylinder or an automatic dispensing device.

   The reagent soon becomes dark brown in color, and yellow chlorine dioxide fills the space above the liquid. Prepared in this way, the reagent may be

*Such a device is the "Cantipette" - dispenser, Chemical Rubber Company, Cleveland, Ohio.

stored for 2-4 hours in the hood at room temperature and used as directed in the delignification schedule.

All unused reagent must be diluted with water and poured into the sewer before the end of each day!

3. Place the wafers of each specimen in a large test tube (25 x 190 mm.) with a 10 ml. Erlenmeyer flask as a loose closure inverted in the mouth of each test tube.
4. Pour 5 ml. of the chlorite reagent (Step 2) into each test tube and place the test tubes in a 1-liter beaker which contains 200 ml. of hot water. (When loaded, the level of water in the beaker should be 1-2 cm. higher than the level of liquid in the test tubes).
5. Place the beaker loaded with the sample tubes on a steam bath and heat the samples for two hours after the temperature inside the test tubes reaches 70-75°. Occasionally, shake the test tube lightly during the heating period.
6. Add 5 ml. of reagent to each sample and continue the heating and agitation for two hours more.
7. Cool the samples in cold water, wash the wafers with water by decantation until free of yellow color, and steep the wafers in 0.2 M sodium hydroxide (Step 1) at room temperature for 30 minutes.
8. Pulp the wafers by the procedure described under "Fiber Washing and Stain" in Revised Method of Fiber Measurement, Cytology Laboratory, I.P.C., April 1967.

Experimental Part

Maceration of Wood. Chlorite Procedures

Part A. Five wafers* were placed in each of six 25 ml. Erlenmeyer flasks (numbered 1 to 6) and lightly closed by loose-fitting glass bulbs.

Sample No. 1 - Sodium chlorite solution (20% w/v), 5 ml., was added to the sample and the mixture was degassed by evacuating (water aspirator) several times. After standing overnight at room temperature, 0.5 ml. of glacial acetic acid was added and the mixture was heated on a steam bath for four hours.** The supernatant was decanted and the wafers were washed with water by decantation. One wafer was removed and was shaken vigorously by hand in approximately 10 ml. of water but the wafer failed to pulp. Partial pulping was accomplished by shaking the wafer in 0.1 N sodium hydroxide.

Sample No. 2 - The procedure was the same as for sample No. 1 except that the evacuation step was omitted. The wafers failed to pulp.

Sample No. 3 - Five milliliters of an acidified chlorite solution (5 ml. of glacial acetic acid added to 100 ml. of 20% (w/v) sodium chlorite) was added. The mixture was allowed to stand overnight at room temperature and was heated on a steam bath for four hours. The wafers were washed with water by decantation. Vigorous shaking in water resulted in nearly complete pulping.

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*Wafers were cut about 1 mm. in thickness with a jackknife from a core (30 mm. in diameter) of aspen supplied by the Genetics Group. The average weight of a 1 mm. wafer of airdry aspen and cottonwood was 0.031 g.

**The temperature of the reaction mixture was 80-88° during the heating period.

Sample No. 4 - The procedure was the same as that for sample No. 3 except that the mixture was not allowed to stand at room temperature before the four-hour heating period. The wafers failed to pulp in water but were readily pulped in 0.1 N sodium hydroxide.

Sample No. 5 - The procedure as described for sample No. 4 was repeated except that air was removed by evacuation before the heating period. As in the case of sample No. 4, the wafers failed to fiberize in water but were readily pulped in 0.1 N sodium hydroxide.

Sample No. 6 - The procedure was the same as that employed for sample No. 5 except that air was removed by evacuation before the mixture was allowed to stand overnight. The wafers were partially pulped in water and completely pulped in 0.1 N sodium hydroxide.

The remaining four wafers from samples No. 1, 2, 4, and 5 were heated for 2 1/2 hours with 5 ml. of the acidified chlorite solution (see above procedures for No. 3). The wafers from sample No. 2 still resisted fiberization in water; samples 1, 4, and 5 were partially pulped. Subsequent shaking with 0.1 N sodium hydroxide resulted in complete pulping of the wafers in samples No. 4 and 5 and nearly complete pulping of No. 1 and 2.

Part B. - Five aspen wafers were placed in a 25 ml. Erlenmeyer flask, 5 ml. of acidified chlorite (as in Part A, Sample 3) was added, air was removed from the mixture by evacuation, and the mixture was heated on a steam bath. After one hour, an additional 5 ml. of acidified chlorite was added and the heating was continued for 1 1/2 hours more. The wafers were washed with water and were shaken vigorously in 10 ml. of water but were not

fiberized. The wafers were partially pulped in 0.1 N sodium hydroxide.

Part C. - Four aspen wafers were placed in each of eight 25 ml. Erlenmeyer flasks and to each was added 5 ml. of acidified chlorite solution* (as in Part A, Sample 3). The samples were divided into two series: one series from which air was removed by evacuation was designated E-1, E-2, E-3, and E-4, and the other series was unevacuated and was designated U-1, U-2, U-3, and U-4. All samples were then heated on a steam bath according to the following schedule:

1. After one hour: - To E-1 and U-1 was added 2 ml. of the chlorite reagent and the heating continued.
2. After two hours: - To E-1 and U-1 another 2 ml. of the chlorite reagent was added, and to E-2 and U-2 5 ml. of reagent was added.
3. After three hours: - To E-1 and U-1 another 2 ml. of chlorite solution was added.

After four hours, all samples were removed from the steam bath, the chlorite solution was decanted, and the samples were washed with water by decantation. The first three samples of each series were allowed to stand in water for 30 minutes and were then shaken vigorously by hand

slightly pulped	E-1, E-3 and U-3
partially pulped	E-2, U-1, U-2
nearly completely pulped	U-4

*Sufficient reagent was made up for the entire experiment.

Samples E-4 and U-4 were allowed to stand in 0.1 N sodium hydroxide for 30 minutes, the solution was decanted, 10 ml. water was added, and the samples were shaken vigorously by hand:

partially pulped	E-4
nearly completely pulped	U-4

Part D. - Fresh cores of Populus tremuloides, T-1, T-2, and T-3, and Populus deltoides, D-1 were supplied by the Genetics Group. The cores were separated into heartwood and sapwood and wafers 1 mm. in thickness were prepared by hand.

Four airdry wafers of each sample were placed in 25 ml. Erlenmeyer flasks, 5 ml. of acidified 20% chlorite solution (Part A, Sample 3) was added, and the mixture was heated on a steam bath. After two hours' heating, another 5 ml. of the chlorite reagent was added and the heating was continued for an additional two hours. The samples were washed with water by decantation and each sample was steeped for 30 minutes in 10 ml. of 0.2 N sodium hydroxide. The alkali was decanted, 10 ml. of water was added, and each was shaken vigorously by hand. All were completely pulped.

Part E. - (1) Alkaline pretreatment. - Four wafers of each sample were placed in 25 ml. Erlenmeyers as in Part D. Sodium hydroxide, 10 ml. of 0.5 N, was added to each and the mixtures were heated on a steam bath for 30 minutes. The alkaline supernatant was decanted, the wafers were washed with water by decantation, and were steeped in 1.5 N acetic acid for 30 minutes. The acid was decanted and the wafers were washed once by decantation.

(2) Chloriting procedure. - To each of the above samples was added 5 ml. of the chlorite reagent (Part A, Sample 3), and the mixtures were heated on a steam bath. After two hours' heating, 5 ml. more of the reagent was added and the heating was continued for a total of four hours. The wafers were washed thoroughly with water and were shaken vigorously with 10 ml. of water. All were partially pulped.

Part F. - Wafers of approximately 10 x 10 x 1 mm. were prepared from specimens of several common pulpwoods. The average weight of the wafers were as listed:

Common name	Code	Average wt. of wafer, g.
Southern pine	SP	0.0769
Southern pine	SP (new)	0.0665
redwood	RW	0.0655
black gum	BG	0.0518
white oak	WO	0.0955

Four wafers of each of 8 samples were placed in 25 ml. Erlenmeyer flasks, 5 ml. of the chlorite reagent (Part A, Sample 3) was added to each and the samples were heated on a steam bath. After two hours, 5 ml. more of reagent was added to each and the heating was continued. The wafers were washed carefully by decantation and were steeped in 10 ml. of 0.2 N sodium hydroxide for 30 minutes. The alkali was decanted, the wafers were washed once with water, and were shaken vigorously in 10 ml. of water. The results are summarized below.

Sample[a]	Degree of Pulping
T-1 and T-3, heartwood; SP, RW, BG	complete
T-2 and D-1, heartwood; WO	nearly complete

[a]Code identified above

Part G. - Four wafers of each 8 samples (heartwood of T-1, T-2, T-3, and D-1; SP-new, RW, WO, BG, were placed in test tubes (25 x 190 mm.) which were loosely closed by inverting a 10 ml. Erlenmeyer in the mouth of each tube. To each tube was added 5 ml. of the chlorite reagent (Part A, Sample 3), the tubes were placed in a 1-liter beaker containing about 200 ml. of water, and the beaker was placed on a steam bath. The temperature of the reaction was determined by placing a thermometer in another tube containing some water, and was found to average approximately 70°. Two hours after the tubes reached a temperature of 75°, 5 ml. of the reagent was added to each tube and the heating was continued for an additional two hours. The wafers were then washed with water by decantation until free of color. One wafer of each sample was shaken vigorously by hand with 30 ml. of water. A second wafer was steeped in 10 ml. of 2% sodium sulfite for 30 minutes at room temperature, washed once with water and then shaken with 30 ml. of water. The remaining 2 wafers were steeped in 10 ml. of 0.2 N sodium hydroxide for 30 minutes, were washed once with water, and then shaken with 30 ml. of water. The results of these treatments are summarized below.

	Treatment		
Sample[a]	None	2% sodium sulfite	0.2 N sodium hydroxide
T-1 heartwood	partially pulped	partially pulped	incompletely pulped
T-2 heartwood	not pulped	slightly pulped	completely pulped

Treatment (continued)

Sample[a]	None	2% sodium sulfite	0.2 N sodium hydroxide
T-3 heartwood	not pulped	slightly pulped	completely pulped
D-1 heartwood	not pulped	not pulped	nearly completely pulped
SP new	partially pulped	partially pulped	completely pulped
RW	completely pulped	completely pulped	completely pulped
WO	slightly pulped	partially pulped	completely pulped
BG	slightly pulped	nearly pulped	completely pulped

[a]For identification of the samples see Parts D and F.

Part H. - Samples of aspen and cottonwood were prepared as follows:

Sample No.	Total number of wafers	Number of each specimen[a]	Sapwood or heartwood	Total weight, g.
1	4	1	sapwood	0.158
2	4	1	heartwood	0.168
3	8	2	sapwood	0.315
4	8	2	heartwood	0.322
5	16	4	sapwood	0.669
6	16	4	heartwood	0.651

[a]Specimens: T-1, T-2, T-3, and D-1 (see Part D)

The samples were placed in test tubes as in Part G, 5 ml. of the chlorite reagent (Part A, Sample 3) was added, and the mixtures were heated on a steam bath at 70-75°. After 45 minutes' heating, 5 ml. of the reagent

was added to No. 5 and 6. After two hours' heating, 5 ml. of reagent was added to each sample and the heating was continued for an additional two hours. The total reagent used was 10 ml. for samples 1-4, and 15 ml. for samples 5 and 6. The wafers were washed with water by decantation until free of color and then were steeped in 10 ml. of 0.2 N sodium hydroxide for 30 minutes at room temperature. The alkali was decanted, the wafers were washed once with water, and were then shaken vigorously in 30 ml. of water. All samples were completely pulped.

Part I. - Acidified sodium chlorite, 5 ml. of approximately 2.75 M $NaClO_2$ in 0.5 N acetic acid, was added to eight samples each consisting of six wafers contained in large test tubes as in Part G.

Sample No.	Species	Code
1	southern pine	SP
2	Austrian pine, compression wood	AP
3	Western red cedar	WRC
4	Western larch	WL
5	Cottonwood, sapwood	D-1-S
6	Cottonwood, heartwood	D-1-h
7	Aspen, sapwood combined sample[a]	T-1-3-S
8	Aspen, heartwood combined sample[a]	T-1-3-h

[a]Two wafers of each T-1, T-2, and T-3 were selected and were identified by marking with soft lead pencil; the pencil marks survived the chloriting treatment.

The mixtures were heated on a steam bath at 70-75°. After one hours' heating,

5 ml. of the reagent was added, the heating was continued for two hours more, a third 5 ml. portion of the reagent was added, and the heating continued for two hours; the total amount of reagent was 15 ml. and the total heating time was five hours. The samples were washed with water by decantation until free of color and were then shaken vigorously by hand in 30 ml. of water. All samples except the Austrian pine compression wood (AP) were completely pulped. Upon steeping the chlorited Austrian pine wafers in 0.2 N sodium hydroxide for 30 minutes at room temperature, complete pulping was accomplished. Examination of the pulps under the microscope revealed that very few fiber bundles survived the pulping procedure.

Part J. - Attempted maceration with peroxyacetic acid (peracetic acid). - Using the general procedure of Leopold (2), the reagent was prepared by mixing 30 ml. of 40% peroxyacetic acid (commercially available) with 50 ml. of 12% aqueous sodium acetate. Four wafers of each of four specimens, D-1, T-1, T-2, and T-3, heartwood, were placed in test tubes as used in part G. The wafers were heated on a steam bath at 70-75° with 10 ml. of the reagent for 60 minutes. One wafer of each sample was removed, washed with water and shaken by hand in water. These wafers showed no tendency to fiberize in water or following a 30-minute steeping period in 0.2 N sodium hydroxide.

The remaining three wafers were heated for 60 minutes in 10 ml. of fresh reagent. After washing and steeping in alkali, wafers from D-1, T-1, and T-2 were beginning to fiberize at the surface of the wafers; a wafer from T-3 was partially pulped. The remaining wafers were heated

for 60 minutes with a third 10-ml. portion of reagent. None of the samples were pulped in water but steeping in diluted alkali resulted in partial pulping of the samples. The cycle was repeated a fourth time on the remaining wafers but pulping in water was incomplete.